Doping evolution of the phonon density of states and electron-lattice interaction in $Nd_{2-x}Ce_xCuO_{4+\delta}$

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We use inelastic neutron scattering to study the evolution of the generalized phonon density of states (GDOS) of the n-type high-T_c superconductor $Nd_{2-x}Ce_xCuO_{4+\delta}$ (NCCO), from the half-filled Mott-insulator ($x = 0$) to the $T_c = 24$ K superconductor ($x = 0.15$). Upon doping the CuO_2 planes in $Nd_2CuO_{4+\delta}$ (NCO) with electrons by Ce substitution, the most significant change in the GDOS is the softening of the highest phonon branches associated with the Cu-O bond stretching and out-of-plane oxygen vibration modes. However, the softening occurs within the first few percent of Ce-doping and is not related to the electron doping induced nonsuperconducting-superconducting transition (NST) at $x \approx 0.12$. These results suggest that the electron-lattice coupling in the n-type high-T_c superconductors is different from that in the p-type materials.

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One of the most remarkable properties of high-transition-temperature (high-T_c) copper-oxide (cuprate) superconductors is their close proximity to an antiferromagnetic (AF) phase. The parent compounds of the high-T_c cuprates are AF insulators characterized by a simple doubling of the crystallographic unit cell in the CuO_2 planes [1]. When holes [2] or electrons [3] are doped into these planes, the long-range AF-ordered phase is destroyed, and the copper-oxide materials become metallic and superconducting with persistent short-range AF spin correlations (fluctuations). Much effort over the past decade has focused on understanding the nature of the interplay between magnetism and superconductivity [1], mainly because spin fluctuations may contribute a major part of the superconducting condensation energy [4, 5]. On the other hand, the role of phonons in the microscopic mechanism of superconductivity is still largely unknown even though phonons in cuprates also display a variety of unusual properties [6, 7, 8, 9, 10]. The key question is whether magnetism and electron-electron correlations alone are sufficient to induce electron pairing that leads to superconductivity in high-T_c cuprates, or electron-lattice coupling also plays an important role.

From the analysis of high-resolution angle-resolved photoemission (ARPES) data in conjunction with those from neutron, optics and local structural probes, Shen and co-workers [11] suggest that phonons must also play an essential role in electron pairing for high-T_c cuprates. The key evidence for electron-lattice coupling, they argue [12], is that the kink (or the change of slope) seen in the electronic dispersion of the hole-doped (p-type) $Bi_2Sr_2CaCu_2O_8$ (Bi2212), $Bi_2Sr_2CuO_6$ (Bi2201), and $La_{2-x}Sr_xCuO_4$ (LSCO) from the ARPES data [13, 14, 15, 16] occurs at an energy ($\sim$70 meV) very close to the phonon anomalies observed by inelastic neutron scattering [7, 8, 9]. These phonon anomalies include the break in the dispersion of the oxygen half-breathing mode in $La_{1.85}Sr_{0.15}CuO_4$ [7] and the abrupt development of new oxygen lattice vibrations near the doping-induced metal-insulator transition (MIT) in the generalized phonon density of states (GDOS) of LSCO [8, 17]. Since the change of slope in the electronic dispersion indicates a dramatic drop in the "quasiparticle" scattering rate [11], their observation in hole-doped cuprate superconductors [13, 14, 15, 16] suggests a strong coupling between the quasiparticles and a sharp collective spin or lattice mode. Although the neutron magnetic resonance [5] could be the collective spin mode coupled to the quasiparticles [16, 18], Shen *et al.* argue that electron-lattice interaction is ultimately responsible for the quasiparticle velocity change and thus is crucial to the high-T_c superconductivity [11, 12]. Furthermore, since the dispersion of the electron-doped superconducting $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ does not have such a kink, the authors [11] predict that the n-type materials have much weaker electron-lattice coupling and thus lower T_c's.

If this hypothesis were correct, one would expect the exotic lattice dynamics seen in the p-type LSCO [7, 8, 9] to be reduced in the n-type $Nd_{2-x}Ce_xCuO_{4+\delta}$ (NCCO) [11]. For LSCO, the abrupt development of the new oxygen lattice vibrations across the doping induced nonsuperconducting-superconducting transition (NST) was interpreted as evidence for strong electron-lattice coupling in the superconducting cuprates that is not present in nonsuperconducting materials [8, 17]. Specifically, the new lattice mode at $\sim$70 meV in the GDOS is believed to be at least partly comprised of the anomalous Cu-O bond-stretching (oxygen half-breathing) mode [8]. Although the GDOS for NCCO with $x = 0, 0.15$ were studied by Lynn and co-workers [19, 20], no systematic doping dependent measurements are available. If the quasiparticle velocity drop seen in the ARPES data of

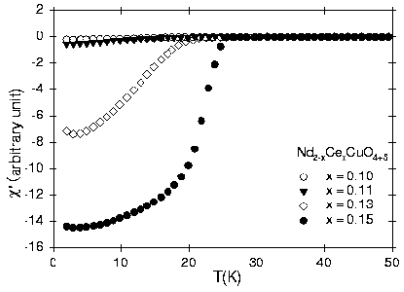

FIG. 1: Temperature dependences of the AC magnetic susceptibility χ' (real part) for the NCCO powder samples used in the neutron measurements. The background was subtracted using the χ' for $x = 0.09$, which shows Curie-Weiss-like behavior down to the lowest temperature measured. The diamagnetic signal first appears for $x \geq 0.11$.

p-type cuprates [11] is related to the anomalous lattice vibrational modes [8], the absence of such a drop in the electron-doped superconducting NCCO with $x = 0.15$ would suggest a weak (or no) phonon anomaly for NCCO.

In this paper, we present inelastic neutron scattering measurements of the GDOS in NCCO spanning electron doping concentrations from the half-filled Mott-insulator ($Nd_2CuO_{4+\delta}$ or NCO) to optimally doped NCCO superconductor ($x \approx 0.15$). Upon doping electrons to the CuO_2 planes by Ce substitution, the most significant change in the GDOS is the anomalous softening of the ~ 70 meV phonon branches associated with the oxygen half-breathing and out-of-plane vibrational modes. However, in contrast to LSCO [8], the anomaly only occurs within the first few percent of Ce-doping and there is no evidence for any new lattice modes in the GDOS across the electron doping induced NST at $x \approx 0.12$. Our results indicate that doping-induced phonon anomalies in hole-doped cuprates are different from these in electron-doped materials, thus suggesting that electron-lattice coupling is unrelated to the superconductivity of NCCO.

Our experiments were performed on the MARI chopper spectrometer at ISIS facility, Rutherford Appleton Laboratory, UK. The detectors on MARI cover a wide scattering angle from 3° to 135°. For the experiments, we used a Fermi chopper to choose an incident beam energy of 110 meV. The energy resolution is between 1-2% of the incident energy. The powder samples were mounted inside the aluminum sample can on the cold head of a helium closed-cycle refrigerator and all measurements were performed at $T = 30$ K. The incident neutron beam size is 5×5 cm^2 and the unexposed area of the sample was covered by Cd sheets. To normalize the scattering from NCCO on an absolute scale, we used the elastic incoherent scattering from a vanadium standard. In addition to measurements at MARI, we have also collected data on the BT-4 filter analyzer spectrometer at the National Institute of Standards and Technology research reactor. To within the error of the measurements, the results of these two experiments are identical.

We prepared the ceramic samples of NCCO with Ce-concentrations of $x = 0.00$, 0.04, 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.15 by the conventional solid state reaction [3]. The as-grown samples have excess oxygen ($\delta > 0$) and are nonsuperconducting. Various annealing procedures have been developed to remove the excess oxygen needed to produce superconductivity. However, the properties of the samples and the resulting electronic phase diagrams are different depending on the details of the annealing procedure used. In the original work of Tagaki *et al.* [3], it was found that samples treated in flowing Ar at temperatures in excess of 1100 °C followed by heating in air at 500 °C produced metallic samples with a sharp superconducting transition. However, it was also found that this procedure resulted in some decomposition of the sample as well as probable loss of Cu from the surfaces of the polycrystalline grains [3]. This procedure also results in the electronic phase diagram showing an abrupt NST around $x = 0.14$ with only half of the superconducting "dome" [3], different from hole-doped LSCO [1]. We have followed the annealing procedure developed by Maple's group [21], where the samples are treated in flowing Ar at temperature of about 900 °C. The resulting phase diagram shows the NST around $x = 0.12$ with the almost complete superconducting dome [21] as compared to the half-dome from [3]. To characterize the materials, bulk magnetization and resistivity measurements were performed for all the samples. Figure 1 shows the doping dependence of the AC susceptibility for $x = 0.1$, 0.11, 0.13, and 0.15. Superconductivity is clearly seen for NCCO with $x \geq 0.13$, thus confirming that the NST in NCCO occurs around $x \approx 0.12$ [21].

In an unpolarized neutron experiment, the major difficulty in obtaining the reliable GDOS is to separate phonons from magnetic scattering. For NCCO, the largest magnetic signal originates from single-ion crystalline electric field (CEF) excitations of the Nd ions [19, 20]. The CEF excitations of NCCO with $x = 0$, and 0.15 have been studied in great detail and their level scheme has peaks around $\hbar\omega \approx$ 12–16, 20.5, 27, and 93.3 meV at low temperatures [22]. We performed careful wave vector (Q) dependent analysis of the excitation intensities at $\hbar\omega = 20.5$, 27, and 93.3 meV for 2 Å^{-1} $< Q <$ 10 Å^{-1}. The outcome confirms the earlier results that these three peaks are magnetic in origin and the phonon cutoff energy of NCCO is around 83 meV [20]. We also checked the strength of the multiple scattering and multi-phonon scattering using the Monte Carlo simulation program MSCAT, but found such multi-phonon scattering contributes negligibly to the total scattering intensity in the energy region of interest ($\hbar\omega \geq 50$ meV). To reduce the magnetic scattering contribution to the GDOS, we replaced the intensities of the 20.5 and 27 meV peaks with scattering from the highest measured wave vectors (9 Å^{-1} $< Q <$ 11 Å^{-1}). Although this procedure may not eliminate all the magnetic intensity, there are no magnetic contributions to the GDOS for 50 meV$\leq \hbar\omega \leq$ 80 meV.

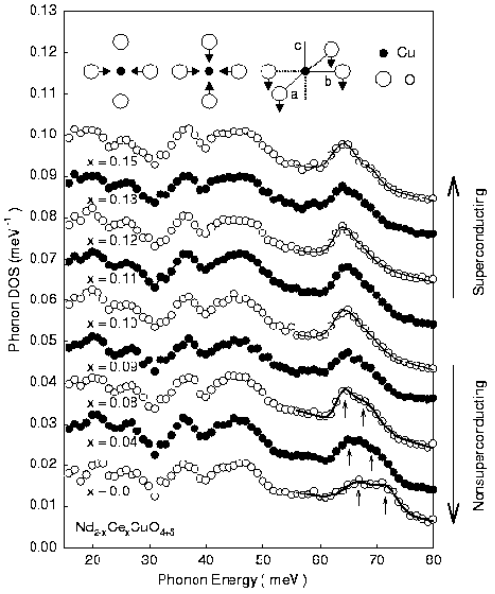

FIG. 2: The GDOS of NCCO as a function of x at $T = 30$ K. Each GDOS is displaced along the vertical axis for clarity and the solid lines are Gaussian fits discussed in the text. The nonsuperconducting-superconducting transition as a function of x is schematically shown on the right. The insets show the polarizations of the oxygen half-breathing (left), breathing (middle), and out-of-plane (right) vibrational modes.

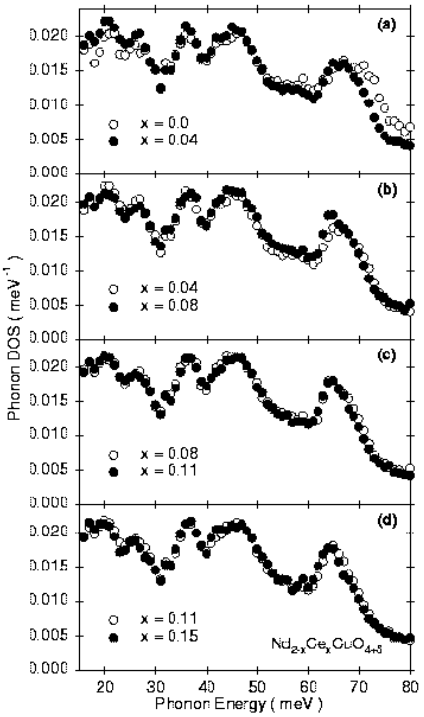

FIG. 3: Comparison of the GDOS of NCCO as a function of electron-doping, x. (a) The GDOS of NCCO for $x = 0.0$, and 0.04; (b) $x = 0.04$, and 0.08; (c) $x = 0.08$, and 0.11; and (d) $x = 0.11$, and 0.15.

After subtraction of the empty aluminum sample can, multiple and multi-phonon scattering, single-phonon GDOS with Q values integrated from 3 to 11 Å^{-1} were calculated by multiplying $\omega/[n(\omega)+1]$, where $n(\omega)$ is the Bose population factor. The total area of each GDOS was then normalized to 1 over the energy range from 15 to 80 meV. Figure 2 shows the GDOS for NCCO with $x = 0.0$, 0.04, 0.08, 0.10, 0.11, 0.12, 0.13, and 0.15. Consistent with previous measurements on NCCO for $x = 0.0$ and 0.15 [19, 20], the spectra contain clear peaks at ∼36, 42, 48, and 65-70 meV. On moving from an insulator to a metal with increasing Ce-concentration, the largest observed effect is the softening and sharpening of the broad ∼70 meV phonon-band in the undoped NCO.

We systematically fit the 70 meV phonon band with two Gaussians on a sloping background for various x. The solid lines in Fig. 2 show the outcome of the fits. Although the precise functional form of the GDOS for the 70 meV phonon band is not known, the systematic Gaussian fits allow a quantitative determination for the magnitude of the phonon softening. For the undoped NCO, the 70 meV mode shows a flattish top and can be best fitted by two Gaussians centered at 67 and 71 meV, respectively. On increasing the Ce-concentration to $x =$ 0.04, the 71 meV mode softens to 67 meV (6% softening) and shows less of a flattish top. Furthermore, the GDOS gains intensity at 65 meV at the expense of the 71 meV peak. At $x = 0.08$, the GDOS peaks more sharply at 65 meV. On further increasing x and across the NST at $x = 0.12$, the GDOS show essentially no change from that for $x = 0.08$ to within the error of the measurements. Figure 3 shows the comparison plots of the GDOS at various x. For NCCO with $0.0 \leq x \leq 0.08$, the 70 meV phonon band shows significant softening while all other modes display no visible change with increasing x (Figs. 3a and 3b). The GDOS for x from 0.08 to 0.15 (Figs. 3c and 3d) overlap completely in the probed energy range ($15 \leq \hbar\omega \leq 80$ meV) and show no changes across the NST.

To understand the atomic displacement patterns of the phonon modes contributing to the 70 meV band in NCO, we consider its experimentally determined phonon dispersion curves [23]. For NCO, the highest energy phonon bands are around 70 meV [23]. These include the highest energy in-plane Cu-O bond-stretching mode with Δ_1-symmetry at $Q = (0.5, 0, 0)$ (the oxygen half-breathing mode) along the $[\zeta, 0, 0]$ direction, the out-of-plane (c-axis polarized) oxygen breathing mode with Λ_1-symmetry along $[0, 0, \zeta]$, and the in-plane oxygen breathing mode with Σ_1-symmetry at $Q = (0.5, 0.5, 0)$ along $[\zeta, \zeta, 0]$. The inset of Fig. 2 shows the oxygen displacement patterns for these three modes. Since these three modes are at ∼70 meV in the dispersion curves [23], the 70 meV peak in the GDOS of NCO must consist, at least partially, of these modes. As a consequence, the electron-doping induced softening in NCCO must also occur in these modes.

In a very recent inelastic X-ray scattering study of longitudinal optical phonons in NCCO with $x = 0.14$, d'Astuto *et al.* discovered anomalous phonon softening in the two highest longitudinal branches associated with the Cu-O bond-stretching and out-of-plane oxygen vibrations [24]. By comparing their data on NCCO with undoped NCO, the authors concluded that strong electron-phonon coupling is also present in electron-doped NCCO. From their work [24], it becomes clear that the significant softening of the 70 meV phonon band with x in Figs. 2 and 3 is mostly due to the softening of the oxygen half-breathing and out-of-plane vibrational modes. For hole-doped LSCO, the oxygen half-breathing modes display anomalous behavior [7, 9] and show up as new lattice modes in the superconducting side of the phase diagram across the NST [8]. While the oxygen half-breathing modes also exhibit anomalous behavior [24] and soften with increasing electron-doping, our results indicate that the softening occurs within the first few percent of Ce-doping in the nonsuperconducting regime and therefore is not associated with the electron doping induced NST in NCCO.

For p-type cuprates, previous investigations have established a clear correlation between superconducting properties of the materials and special features of the phonon spectrum. While such correlation is seen as anomalous phonon modes across the NST in LSCO [8], systematic studies of the GDOS in $YBa_2Cu_3O_{6+x}$ show that the phonon cut-off energy softens across the NST and is closely related to T_c (see Fig. 41 of [6]). In general, these phonon anomalies are related to the dielectric screening properties of metals and thus suggest a strong electron-lattice coupling in the superconductivity of the p-type materials. Although phonon softening is also observed in the n-type NCCO, our data indicate that these anomalies occur in the nonsuperconducting regime and are not directly related to the NST. Therefore, it becomes clear that the electron-lattice coupling in the electron-doped NCCO is different from that in the hole-doped materials.

It is interesting to compare our results with that of the ARPES on NCCO. In principle, the strong electron-lattice coupling and large softening of the optical oxygen vibrational modes in NCCO with $x = 0.04$ should reveal themselves as distinctive features in the ARPES spectra [11]. If the kink in the electronic band dispersion in the hole-doped materials is due to the anomalous softening of the 70 meV oxygen half-breathing mode [11], its absence in electron-doped NCCO would suggest no softening of such oxygen modes in NCCO. Clearly, this is inconsistent with the results of [24] and the present work. On the other hand, if the kink in the ARPES spectra is not related to the softening of the 70 meV modes but to the changes of such modes across the hole- (electron-) induced NST, our data would be consistent with a weak electron-lattice coupling in NCCO. An unambiguous test of this idea will require comparison of the neutron data with the doping dependence of the electronic structure of NCCO. Although systematic ARPES investigations have been carried out very recently on NCCO [25], the evolution of the electronic dispersions across the MIT or NST is unavailable and therefore cannot be compared yet with the neutron results.

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